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(21) International Application Number: PCT/US96/02300 (22) International Filing Date: 20 February 1996 (20.02.96) (30) Priority Data: 08/401,514 10 March 1995 (10.03.95) US (71) Applicants: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). HOECHST AKTIENGESELLSCHAFT [DE/DE]; Zentrale Patentabteilung, Postfach 80 03 20, D-65926 Frankfurt am Main 80 (DE). (72) Inventor: BRINEN, Jeffrey, Lawrence; 2109 Olympic Drive, League City, TX 77573 (US). (74) Agents: SCHMIDT, C., Paige et al.; Exxon Chemical Com- pany, P.O. Box 2149, Baytown, TX 77522-2149 (US).		(81) Designated States: BR, CA, CN, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: METHOD FOR PRODUCING A PREPOLYMERIZED CATALYST**(57) Abstract**

A method for controlling fouling in a prepolymerization reactor is disclosed and comprises combining a supported metallocene catalyst system, an alpha olefin monomer feed, and added hydrogen under suitable prepolymerization reaction conditions. This method is also useful for the control of agglomeration during a prepolymerization reaction.

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Title: Method for Producing a Prepolymerized Catalyst

5 This is a Continuation-in-Part of U.S. Application Serial No. 08/174,498, filed December 28, 1993.

Field of the Invention:

10 This invention relates generally to a catalyst system for the polymerization of olefins, more specifically, to the prepolymerization of supported catalyst systems and the use thereof.

Background of the Invention:

15 Supported metallocene catalyst systems are used primarily in slurry, bulk liquid, and gas-phase polymerization processes. In general the catalyst systems and various methods to make them from transition metal components and activators are well known and exploited. These supported catalyst systems may be subjected to a prepolymerization step to enhance performance. Prepolymerization often confers the advantages of reduced fines formation, and superior product properties such as
20 better granular morphology, higher bulk density, and improved granule flow properties. See EPA 447,071.

EPA 279,863 discloses a method for preparing a supported, prepolymerized metallocene catalyst system. The specific metallocene used is Cp_2ZrCl_2 , which is supported on silica and prepolymerized with ethylene. EPA
25 279,863 suggests using a molecular weight controlling agent such as hydrogen to produce a prepolymer having certain intrinsic viscosities. Applicants have found that certain low activity catalyst systems containing certain metallocenes such as Cp_2ZrCl_2 may be supported and prepolymerized without fouling the prepolymerization reactor and without producing agglomerated catalyst particles.

30 However, other catalyst systems, such as high activity catalyst systems tend to foul the prepolymerization reactor and/or produce agglomerated catalyst system particles. It would be highly desirable to have an efficient method for using such catalyst systems without fouling and agglomeration in the prepolymerization reactor.

35 Summary of the Invention:

This invention relates to a method for yielding a non-fouling, non-agglomerating supported prepolymerized catalyst system. The invention involves use of hydrogen to control the fouling and agglomeration observed during

prepolymerization of high activity supported catalyst systems which tend to foul during prepolymerization.

The invention relates to a method for controlling fouling in a prepolymerization reactor, said method comprising the step of combining:

- 5 (a) a supported metallocene catalyst system having an activity greater than about 100,000 g/g/hr.;
- (b) at least one alpha olefin monomer feed; and,
- (c) added hydrogen

10 under suitable prepolymerization reaction conditions. Ethylene and/or propylene are used as the preferred monomer feed for the prepolymerization of these supported catalysts.

Preferably, the metallocene catalyst system of this invention has a known tendency to foul a prepolymerization reactor and/or produce agglomerated catalyst system particles upon prepolymerization. Even more preferably, the metallocene
15 catalyst system has an activity of from about 100,000 g polymer/g metallocene/hr to about 1,000,000 g polymer/g metallocene/hr. preferably greater than 150,000 g polymer/g metallocene/hr., even more preferably greater than 200,000 g polymer/g metallocene/hr. or from about 150,000 g polymer/g metallocene/hr to about
20 900,000 g polymer /g metallocene/hr., preferably from about 200,000 g polymer /g metallocene/hr to about 500,000 g polymer/g metallocene/hr..

Hydrogen is generally added in an amount of from about 0.1 to about 10 mole percent relative to the monomer feed rate. The monomer feed is generally added at a rate of about 0.1 to about 10 g olefin/g catalyst solid/hour. Suitable
25 prepolymerization reaction conditions are typically run at low temperatures, for example in the range of from about -20°C to about 40°C, preferably from about -10°C to about 20°C, most preferably from about 0°C to about 10°C.

Still further, the invention relates to use of the prepolymerized catalyst system formed by the method described herein and further relates to a method for
30 controlling agglomeration of catalyst particles during the prepolymerization procedure.

Detailed Description of the Preferred Embodiments

Prepolymerization reactor fouling and catalyst agglomeration which are observed during the prepolymerization of some metallocene catalyst systems,
35 particularly high activity metallocene catalyst systems, can be minimized or eliminated by the use of hydrogen during prepolymerization. In a preferred embodiment, a supported metallocene catalyst system having high activity,

monomer feed containing at least one alpha olefin, and added hydrogen are combined in a prepolymerization reactor, under suitable prepolymerization reaction conditions to control fouling and agglomeration of the supported catalyst system during prepolymerization. A further embodiment of the invention relates to the use
5 of the prepolymerized supported catalyst system prepared by the method described herein for the polymerization of olefins to polyolefins.

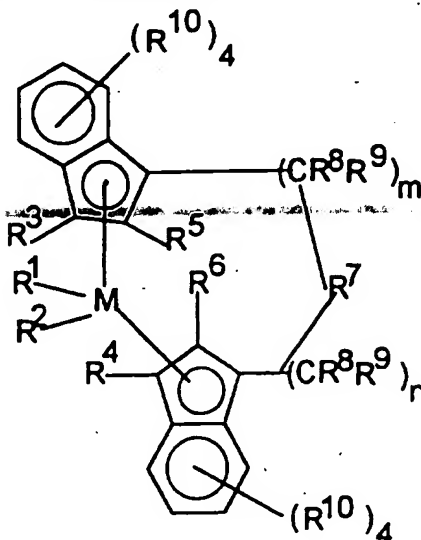
For purposes of this application and claims, the phrase "added hydrogen" is defined to mean hydrogen which is purposely added during the prepolymerization reaction. Hydrogen which may be generated in-situ is excluded from this
10 definition. Fouling is defined occurs when material sticks to the walls of the reactor. Agglomeration occurs when the catalyst system particles stick to each other. Fouling and agglomeration may or may not occur together.

As used herein, "metallocene" and "metallocene catalyst component" mean those bulky ligand transition metal compounds represented by the formula:
15



wherein Cp is a cyclopentadienyl ring or derivative thereof, M is a Group 4, 5, or 6 transition metal and/or a metal from the lanthanide or actinide series, R is a
20 hydrocarbyl group or hydrocarboxy group having from 1 to 20 carbon atoms, X is a halogen, and $m=1-3$, $n=0-3$, $q=0-3$, and the sum of $m+n+q$ is equal to the oxidation state of the transition metal. The metallocene may be bridged or unbridged, and include heteroatoms in the structure. In addition, one or more bulky ligands may be π -bonded to the transition metal atom. Other ligands may be
25 bonded to the transition metal, for example, a leaving group, such as but not limited to hydrocarbyl, hydrogen or any other univalent anionic ligand. Non-limiting examples of metallocenes and metallocene catalyst systems are discussed in for example, U.S. Patent Nos. 4,530,914, 4,952,716, 5,124,418, 4,808,561, 4,897,455, 5,278,264, 5,278,119, 5,304,614 all of which are herein fully
30 incorporated by reference. Also, the disclosures of EP-A- 0 129 368, EP-A-0 591 756, EP-A-0 520 732, EP-A- 0 420 436, WO 91/04257 WO 92/00333, WO 93/08221, and WO 93/08199 are all fully incorporated herein by reference. The preferred transition metal component of the catalyst system of the invention are those of Group 4, particularly, zirconium, titanium and hafnium. The transition
35 metal may be in any oxidation state, preferably +3 or +4 or a mixture thereof.

Preferred metallocenes comprise a Group 4, 5, or 6 transition metal, biscyclopentadienyl derivatives, preferably bridged bis-indenyl metallocene components having the following general structure:



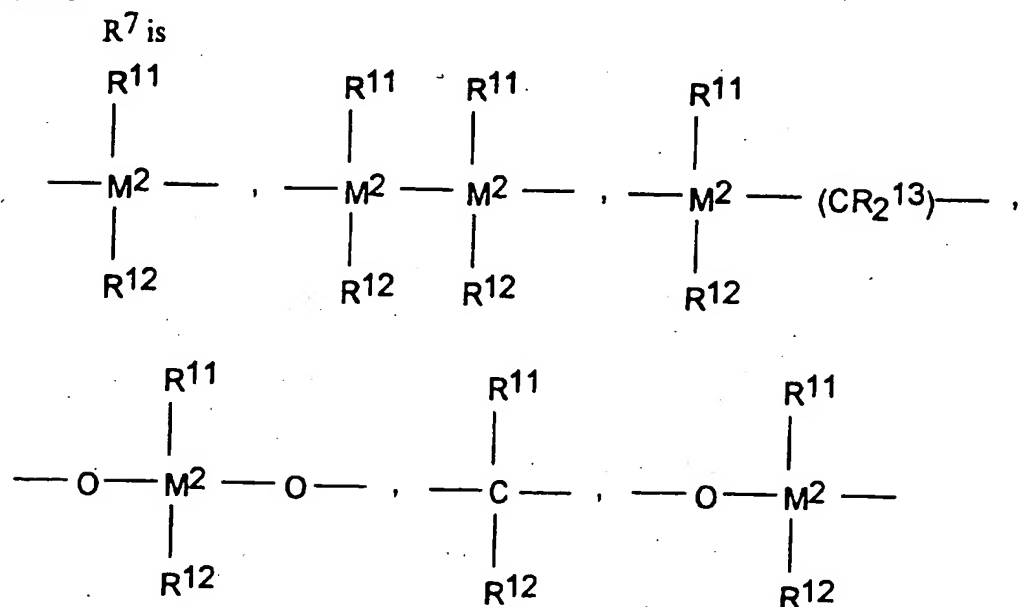
- 5 wherein M is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium;

- 10 R^1 and R^2 are identical or different, are one of a hydrogen atom, a C_1 - C_{10} alkyl group, preferably a C_1 - C_3 alkyl group, a C_1 - C_{10} alkoxy group, preferably a C_1 - C_3 alkoxy group, a C_6 - C_{10} aryl group, preferably a C_6 - C_8 aryl group, a C_6 - C_{10} aryloxy group, preferably a C_6 - C_8 aryloxy group, a C_2 - C_{10} alkenyl group, preferably a C_2 - C_4 alkenyl group, a C_7 - C_{40} arylalkyl group, preferably a C_7 - C_{10} arylalkyl group, a C_7 - C_{40} alkylaryl group, preferably a C_7 - C_{12} alkylaryl group, a
15 C_8 - C_{40} arylalkenyl group, preferably a C_8 - C_{12} arylalkenyl group, or a halogen atom, preferably chlorine;

R^3 and R^4 are hydrogen atoms;

- R^5 and R^6 are identical or different, preferably identical, are one of a
20 halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1 - C_{10} alkyl group, preferably a C_1 - C_4 alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, preferably a C_6 - C_8 aryl group, a C_2 - C_{10} alkenyl group, preferably a C_2 - C_4 alkenyl group, a C_7 - C_{40} -arylalkyl group, preferably a C_7 - C_{10} arylalkyl group, a C_7 - C_{40} alkylaryl group, preferably a C_7 - C_{12} alkylaryl group, a C_8 - C_{40} arylalkenyl group, preferably a C_8 - C_{12} arylalkenyl
25 group, a $-NR_2^{15}$, $-SR^{15}$, $-OR^{15}$, $-OSiR_3^{15}$ or $-PR_2^{15}$ radical, wherein R^{15} is one of a halogen atom, preferably a chlorine atom, a C_1 - C_{10} alkyl group,

preferably a C₁-C₃ alkyl group, or a C₆-C₁₀ aryl group, preferably a C₆-C₉ aryl group;



5

=BR¹¹, =AlR¹¹, -Ge-, -Sn-, -O-, -S-, =SO, =SO₂, =NR¹¹, =CO, PR¹¹, or =P(O)R¹¹;

wherein:

R¹¹, R¹² and R¹³ are identical or different and are a hydrogen atom, a halogen
 10 atom, a C₁-C₂₀ alkyl group, preferably a C₁-C₁₀ alkyl group, a C₁-C₂₀ fluoroalkyl group, preferably a C₁-C₁₀ fluoroalkyl group, a C₆-C₃₀ aryl group, preferably a C₆-C₂₀ aryl group, a C₆-C₃₀ fluoroaryl group, preferably a C₆-C₂₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, preferably a C₁-C₁₀ alkoxy group, a C₂-C₂₀ alkenyl group, preferably a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl
 15 group, preferably a C₇-C₂₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₂₂ arylalkenyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₂₀ alkylaryl group or R¹¹ and R¹², or R¹¹ and R¹³, together with the atoms binding them, can form ring systems;

20 M² is silicon, germanium or tin, preferably silicon or germanium, most preferably silicon;

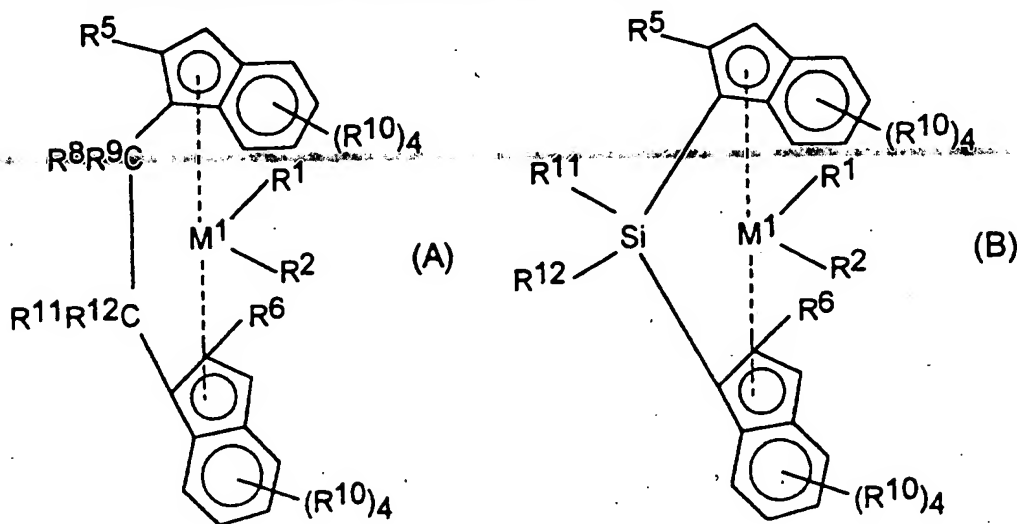
R⁸ and R⁹ are identical or different and have the meanings stated for R¹¹;

m and n are identical or different and are zero, 1 or 2, preferably zero or 1, m plus n being zero, 1 or 2, preferably zero or 1; and

25 the radicals R¹⁰ are identical or different and have the meanings stated for R¹¹, R¹² and R¹³. Two adjacent R¹⁰ radicals can be joined together to form a ring system, preferably a ring system containing from about 4-6 carbon atoms.

Alkyl refers to straight or branched chain substituents. Halogen (halogenated) is fluorine, chlorine, bromine or iodine atoms, preferably fluorine or chlorine.

Particularly preferred metallocenes are compounds of the structures:



wherein:

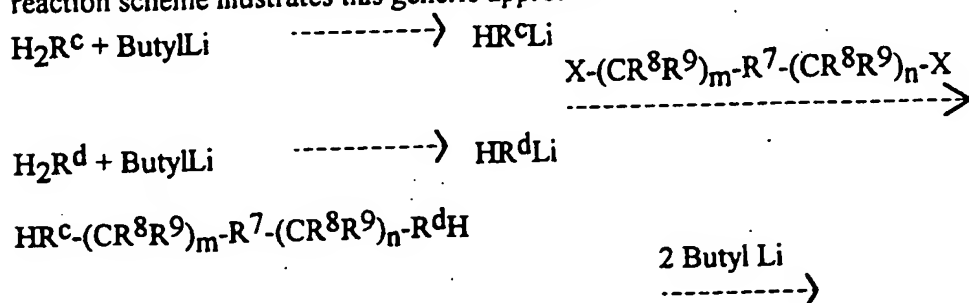
M^1 is Zr or Hf, R^1 and R^2 are methyl or chlorine, and $R^5, R^6, R^8, R^9, R^{10}, R^{11}$ and R^{12} have the above-mentioned meanings.

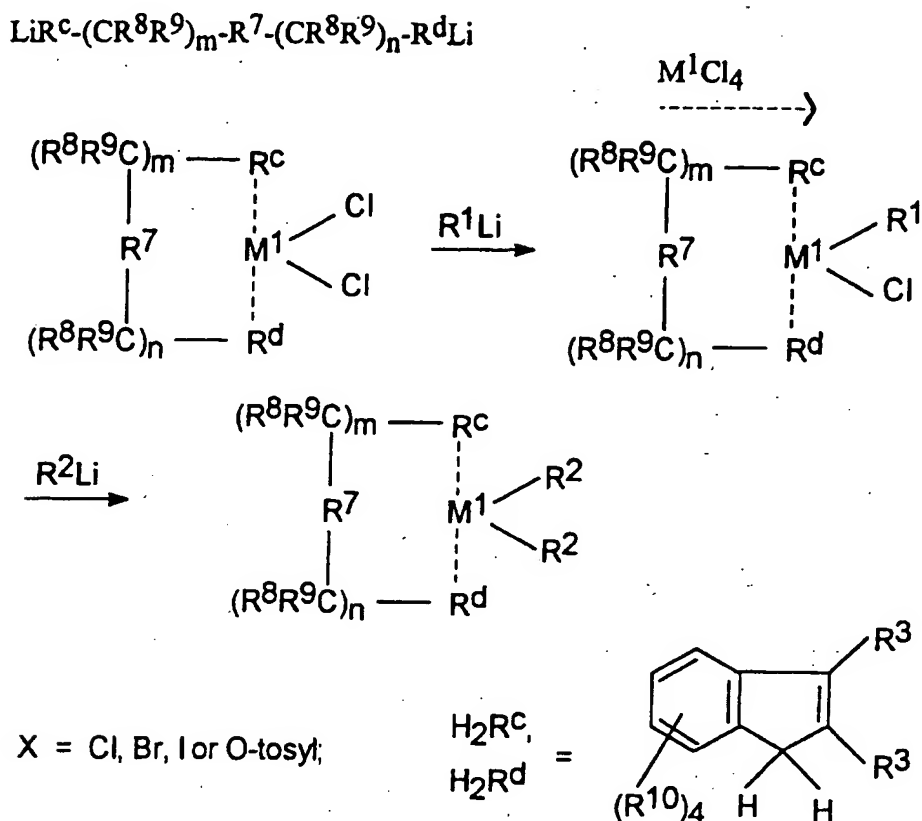
The chiral metallocenes are used as a racemate for the preparation of highly isotactic polypropylene copolymers.

It is also possible to use either the pure R or S form. An optically active polymer can be prepared with these pure stereoisomeric forms. It is preferred that the meso form of the metallocenes be removed to ensure the center (i.e., the metal atom) provides stereoregular polymerization.

Separation of the stereoisomers can be accomplished by known literature techniques. For special products it is also possible to use rac/meso mixtures.

Generally, the metallocenes are prepared by a multi-step process involving repeated deprotonations/metallations of the aromatic ligands and introduction of the bridge and the central atom by their halogen derivatives. The following reaction scheme illustrates this generic approach:





- 5 The reader is referred to the Journal of Organometallic Chem., volume 288, (1958), pages 63-67, and EP-A- 320762, for preparation of the metallocenes described, both references are herein fully incorporated by reference.

Illustrative but non-limiting examples of metallocenes include:

- Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl)ZrCl₂
- 10 Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl)ZrCl₂;
- Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)ZrCl₂;
- Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl₂;
- Dimethylsilandiylbis (4-naphthyl-1-indenyl)ZrCl₂,
- Phenyl(Methyl)silandiylbis(2-methyl-4-phenyl-1-indenyl)ZrCl₂,
- 15 Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl₂,
- Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl₂,
- Dimethylsilandiylbis(indenyl)ZrCl₂,
- Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl₂,
- Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl)ZrCl₂,
- 20 Phenyl(Methyl)silandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
- 1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
- 1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
- Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,

- Dimethylsilandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-ethyl-4-methyl-1-indenyl)ZrCl₂,
5 Dimethylsilandiylbis(2,4-dimethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂,
~~Phenyl(Methyl)silandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,~~
Phenyl(Methyl)silandiylbis(2-methyl-4,5-(methylbenzo)-1-indenyl)ZrCl₂,
10 Phenyl(Methyl)silandiylbis(2-methyl-4,5-(tetramethylbenzo)-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
1,2-Butandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
15 1,2-Ethandiylbis(2,4,7-trimethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-1-indenyl)ZrCl₂,
Diphenylsilandiylbis(2-methyl-1-indenyl)ZrCl₂,
20 1,2-Butandiylbis(2-methyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-ethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-5-t-butyl-1-indenyl)ZrCl₂,
25 Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl)ZrCl₂, and the like.

The preferred metallocene catalyst components of this invention are described in detail in U.S. Patent Nos. 5,149,819, 5,243,001, 5,239,022, 5,296,434 and 5,276,208 all of which are herein fully incorporated by reference. Also preferred are those catalysts described in U.S. Patent No. 5,296,434 herein fully
30 incorporated by reference.

The metallocenes discussed above are activated to form the active catalyst system or "metallocene catalyst system." The metallocene activator may be any compound or component which can activate a bulky ligand transition metal compound or a metallocene as defined above. Alumoxane may be used as the
35 activator as well as ionizing activators, neutral or ionic. For example, compounds such as tri (n-butyl) ammonium bis(pentafluorophenyl) boron, which ionize the neutral metallocene compound, may be used as the activator. Examples of ionizing

activators and methods of their production and use may be found in U.S. Patent Nos. 5,153,157; 5,198,401; 5,241,025; 5,278,119; and 5,384,299 herein fully incorporated by reference.

Alumoxane is represented by the formula: $R-(Al(R)-O)_n-AlR_2$ for
5 oligomeric linear alumoxanes and $(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane wherein n and m are 1 to 40, preferably 3 to 20, and R is a C_{1-8} alkyl group or R is an C_{6-18} aryl group, or hydrogen, preferably a methyl group, or R can be mixtures of alkyl and aryl substituents. Alumoxane or methylalumoxane can be prepared by a variety of known processes such as those illustrated in, for example, U.S. Patent
10 No.s 4,665,208; 4,952,540; 5,091,352; 5,206,199; 5,204,419; 4,874,734; 4,924,018; 4,908,463; 4,968,827; 5,308,815; 5,329,032; 5,248,801; 5,235,081; 5,157,137; and 5,103,031 (each incorporated herein by reference).

Descriptions of ionic catalysts for coordination polymerization comprised of metallocene cations activated by non-coordinating anions appear in the early
15 work in EP-A-0 277 003, EP-A-0 277 004 and US patent 5,198,401 and WO-A-92/00333 (each incorporated herein by reference). These teach a preferred method of preparation wherein metallocenes (bisCp and monoCp) are protonated by an anionic precursors such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced by the non-coordinating anion.

20 The term "noncoordinating anion" means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will
25 not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the metallocene cation in the sense of balancing its ionic charge in a +1 state, yet retain sufficient lability to permit
30 displacement by an ethylenically or acetylenically unsaturated monomer during polymerization. Additionally, the anions useful in this invention will be large or bulky in the sense of sufficient molecular size to largely inhibit or prevent neutralization of the metallocene cation by Lewis bases other than the polymerizable monomers that may be present in the polymerization process.
35 Typically the anion will have a molecular size of greater than or equal to about 4 angstroms.

The use of ionizing ionic compounds not containing an active proton but capable of producing the both the active metallocene cation and an noncoordinating anion is also known. See, EP-A-0 426 637 and EP-A- 0 573 403 (incorporated herein by reference). An additional method of making the ionic
5 catalysts uses ionizing anionic pre-cursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the metallocene compounds, for example the use of tris(pentafluorophenyl) boron. See EP-A-0 520 732 (incorporated herein by reference). Ionic catalysts for addition polymerization can also be prepared by oxidation of the metal centers of transition metal
10 compounds by anionic pre-cursors containing metallic oxidizing groups along with the anion groups, see EP-A-0 495 375 (incorporated herein by reference).

Where the metal ligands include halogen moieties (for example, bis-cyclopentadienyl zirconium dichloride) which are not capable of ionizing abstraction under standard conditions, they can be converted via known alkylation
15 reactions with organometallic compounds such as lithium or aluminum hydrides or alkyls, alkylalumoxanes, Grignard reagents, etc. See EP-A-0 500 944 and EP-A1-0 570 982 for *in situ* processes describing the reaction of alkyl aluminum compounds with dihalo-substituted metallocene compounds prior to or with the addition of activating anionic compounds.

20 Methods of supporting ionic catalysts comprising metallocene cations and noncoordinating anions are described in WO91/09882, WO 94/03506 and in co-pending U.S. Ser. No. 08/248,284, filed August 3 1994 (each incorporated herein by reference). The methods generally comprise either physical adsorption on traditional polymeric or inorganic supports that have been largely dehydrated and
25 dehydroxylated, or using neutral anion precursors that are sufficiently strong Lewis acids to activate retained hydroxy groups in silica containing inorganic oxide supports such that the Lewis acid becomes covalently bound and the hydrogen of the hydroxy group is available to protonate the metallocene compounds.

Generally, activation is carried out in a solution containing dissolved
30 activator. When alumoxane is used as the activator the concentration, of alumoxane in the solution may range from about 1% by weight up to the saturation limit, preferably, from about 5% to about 30% by weight in each case based on the entire solution. The metallocene is dissolved in this solution such that the concentration of metallocene in solution may be up to the saturation limit.

35 Preferably the atomic ratio of the alumoxane aluminum atom to the metallocene metal atom is from about 1 to about 1000, preferably about 10 to about 700, more preferably about 100 to about 400. The time required for activation may be from

about 5 minutes or more, preferably from about 5 to about 60 minutes at a temperature ranging from about -78°C to about 100°C, preferably from about 0°C to about 40°C.

Alternatively, ionic activators may be used as described above in which case the activation may be carried out in solution at a temperature ranging from about -100°C to about 300°C, preferably from about 0°C to about 100°C. The time for reaction may range from about 10 seconds to about 60 minutes depending upon variables such as reaction temperature and choice of reactants.

The prepolymer formed during the prepolymerization may be a homopolymer or copolymer. If a copolymer is desired, monomer mixtures, such as ethylene-propylene, ethylene-butene or ethylene-hexene mixtures may be introduced into the prepolymerization reactor. Generally, the prepolymer is made up of one or more alpha olefins having between 2 and about 20 carbon atoms. Preferably the principle olefin contains between 2 and about 10 carbon atoms, most preferably 2 or 3 carbon atoms.

In a preferred embodiment, the hydrogen is generally added in an amount between about 0.1 to about 10 mole percent relative to the monomer feed rate under prepolymerization conditions. Hydrogen is preferably added at about 0.5 to about 6 mole percent and most preferably from about 1 to about 3 mole percent relative to the monomer feed rate.

In a preferred embodiment the olefin feed or monomer is polymerized onto the supported, solid, catalyst system thereby forming the prepolymer during the prepolymerization reaction. The olefin feed is preferably added during prepolymerization at a rate of from about 0.1 to about 10 g olefin/g catalyst solid/hour, more preferably from about 0.1 to about 5 g olefin/g catalyst solid/hour, and most preferably at a rate of from about 0.5 to about 1.5 g olefin/g catalyst solid/hour. Prepolymer contents of from about .05 to about 30 g prepolymer/g catalyst is an acceptable and general amount formed during the prepolymerization reaction. Preferably an amount of from about 0.1 to about 20 g prepolymer/g catalyst is formed, and most preferably an amount in the range of about .2 to about 10 g prepolymer/g catalyst is formed onto the supported catalyst system during the prepolymerization process.

Experiments for this invention were generally run with a calculated prepolymerization rate of about 0.5 to about 1.0 g prepolymer/g catalyst/hour using ethylene as the monomer. This rate resulted in no fouling or agglomeration of the prepolymerized supported catalyst system. Additionally, the prepolymerized catalyst had a granular morphology and was free flowing.

Preferred prepolymerization reaction conditions generally include low temperatures, for example, in the range of about -20 to about 40° C. Preferably the temperature during prepolymerization is in the range of about -10 to about 20° C. and most preferably is in the range of about 0 to about 10 ° C. Solvents suitable for use during the prepolymerization include inert hydrocarbons such as isopentane, hexane, and the like. A solvent is generally chosen so as it does not interact with the supported catalyst system. The reaction time is dependent upon the amount of prepolymer being formed on the catalyst.

In an embodiment of the invention, the supported catalyst system is a metallocene-alumoxane catalyst system supported on silica in accordance with the support technique described in US 5,240,894, incorporated by reference. The support technique described in US '894 involves production of a metallocene-alumoxane reaction product which is then placed on dehydrated silica and thoroughly dried prior to use. In an alternate embodiment, the catalyst system may be supported in accordance with that taught in US 4,937,301 or 5,008,228 which involves adding the metallocene, and trimethylaluminum to a water impregnated or wet silica support. In a further alternate embodiment the catalyst may be supported in accordance with US 4,808,561 which describes placing the metallocene on a methylalumoxane coated silica support. Any support technique generally useful for producing catalyst for use in gas phase or slurry polymerization is acceptable for the purposes of this invention. For example, support techniques described in U.S. Pat. Nos. 4,808,561; 4,897,455; 4,937,301; 4,937,217; 4,912,075; 5,008,228; 5,086,025; 5,147,949; and 5,240,894 may be employed, all references incorporated by reference. The examples herein describe supporting a catalyst in accordance with the techniques described in U.S. Pat. Nos. 5,240,894; 4,937,301; 4,808,561. The examples of the invention illustrate that the invention works well with a variety of techniques.

The invention is further illustrated by the following non limiting examples. All solvents were purchased from commercial sources, nitrogen purged and dried over activated molecular sieves. Unsubstituted Cp_2ZrCl_2 was purchased from commercial sources. Alumoxane solutions were purchased as 10-30 wt % solutions. Silica is Davison 948 (average particle = 50 microns) dehydrated at either 200 or 800°C under flow of nitrogen.

35 Examples

Comparative Example 1- Preparation of supported Cp_2ZrCl_2 /methylalumoxane (MAO) catalyst system. The support technique

employed was in accordance with US 4,808,561. The activity of this catalyst system (unsupported, methylalumoxane activated) is estimated to be 15,000 g polymer/ g metallocene/ hour.

5 In an inert atmosphere dry box, 10.0 g of calcined silica obtained by calcining at 200° C for 4 hours, 12.5 g of methyl alumoxane solution (MAO, commercially available from Ethyl Corp. as 30 wt.% in toluene, Lot # 004667-3), and 25 cm³ of toluene were combined in a 200 ml flask while stirring. This mixture was heated to 55°C, and allowed to mix for 1 hour. In another flask, 0.152 g of Cp₂ZrCl₂ metallocene was dissolved in 10 cm³ of hexane. The metallocene
10 solution was added to the silica/MAO mixture under slow stirring. After 30 minutes, the heat was removed, and the mixture was stirred for another 30 minutes. When the stirring was stopped, the solids settled to the bottom of the flask, and the supernatant liquid was decanted. Another 30 cm³ of hexane was added to the flask, and the mixture was stirred for 15 minutes. The solids were allowed to
15 settle, the supernatant liquid was decanted, and the catalyst solids were dried under vacuum until no further change in weight was observed. The yield of supported catalyst system was 12.6 g.

Comparative Example 2 - Prepolymerization of the catalyst system of Comparative Example 1 - In an inert atmosphere dry box, 4.0 g of the supported
20 catalyst of Example 1 were placed in a 946 cm³ (1 quart) glass reaction vessel with 150 cm³ of isopentane. The reactor head, equipped with an overhead stirrer and thermocouple, was installed, and the reactor was pressure tested at 1.38 bar (20 psi). The reactor was removed from the drybox, and connected to an ethylene feed manifold. The feed manifold was purged with nitrogen, the stirrer was
25 started, and the reactor was placed in a silicon oil/dry ice bath in order to maintain the desired reaction temperature of 0°C (32 °F). Once the reaction temperature was established, ethylene feed was introduced to the reactor. The rate of ethylene addition was set such that the rate of prepolymerization was 1.0 g ethylene per g catalyst solids per hour. Ethylene feed to the reactor was stopped after one hour
30 reaction time. During the 1 hour duration of the experiment, no fouling or agglomeration of the solids in the reactor was observed. Upon completion of the ethylene addition, the reactor was isolated from the feed manifold, taken back inside the dry box, and the prepolymerized catalyst system solids were collected by suction filtration over a medium porosity fritted funnel. When dry, the
35 prepolymerized catalyst system was a granular, free-flowing solid. The reactor walls and agitator were clean and free of fouling. The yield of prepolymerized catalyst system was 7.0 g.

Example 3- Preparation and prepolymerization without hydrogen of supported $(1,3\text{-MeBuCp})_2\text{ZrCl}_2$ /MAO catalyst system. The support technique employed was in accordance with US 4,937,301. The activity of this catalyst system (unsupported, methylalumoxane activated) is estimated to be 43,500 g polymer/ g metallocene/ hour.

The metallocene is identified generically in EP 552946 and may be prepared in accordance with that described in EP 552946.

~~The prepolymerization procedure of Example 2 was repeated using 2.5~~
grams of supported $(1,3\text{-MeBuCp})_2\text{ZrCl}_2$, 75 cm³ of isopentane, and a
10 prepolymerization rate 0.67 g ethylene per g catalyst solids per hour. After 30 minutes of ethylene addition, an accumulation of solids was observed on the walls of the reactor. After 32 minutes, the solids in the reactor agglomerated severely. Ethylene feed was stopped after 90 minutes. The solids were collected by suction filtration. The solids contained agglomerates as large as 1.8 mm in diameter, and
15 were not free-flowing. The yield of prepolymerized catalyst system was 4.4 g.

Example 4- Prepolymerization with hydrogen of supported $(1,3\text{-MeBuCp})_2\text{ZrCl}_2$ /MAO catalyst system.

The procedure of Example 3 was repeated with the exception that the monomer feed stream to the reactor was changed from pure ethylene to a mixture
20 of 6 mol% hydrogen in ethylene. No fouling or agglomeration of the solids in the reactor were observed. After 90 minutes, the feed to the reactor was stopped. The prepolymerized catalyst was collected by suction filtration. The product was a granular, free-flowing solid, with no evidence of the agglomerates observed with the catalyst made in Example 3. The yield of prepolymerized catalyst was 4.1 g.

25 Example 5- Preparation of supported dimethylsilyl(2-Me,4,5-benzoindenyl)₂ZrCl₂

The metallocene catalyst component was prepared as follows:

Diethyl methyl (2-naphthylmethyl) malonate (1)

30 5.15 g (224 mmol) of sodium were dissolved in 150 ml of absolute ethanol, while heating, and 37.3 ml (217 mmol) of diethyl methylmalonate were added at room temperature. A solution of 50 g (217 mmol) of 2-bromomethylnaphthalene (96% pure) in 270 ml of ethanol was slowly added dropwise at 0°C, and the mixture was heated under reflux for a further 4 to 5 hours. It was poured onto ice-
35 water and extracted with ethyl acetate. The combined organic phases were dried with sodium sulfate and evaporated. After drying under an oil pump vacuum, the

oily residue was stirred with hexane at 0°C, whereupon 55 g (81%) of the compound 1 crystallized.

Synthesis of 2-Methyl-3-naphthylpropionic acid (2)

5 A solution of 23.7 g (422 mmol) of potassium hydroxide in 50 ml of water was added to 33.2 g (105 mmol) of the compound 1 in 70 ml of ethanol, and the mixture was heated under reflux for 4 hours. After the solvent had been stripped off, the solid residue was taken up in ethyl acetate, water was added and the pH was brought to 1 with hydrochloric acid. The aqueous phase was extracted several
10 times with ethyl acetate. After drying over magnesium sulfate, the combined organic phases were evaporated completely. The residue was stirred with hexane for crystallization. For decarboxylation, the beige-colored solid was heated at 175°C until the evolution of gas had ended. 21 g (94%) of the product 2 were obtained as a beige-colored solid.

15

Synthesis of 2-Methyl-6,7-benzoindan-1-one (3)

22 ml of thionyl chloride were added to 21 g (98 mmol) of the compound 2, with exclusion of moisture, and the mixture was heated under reflux for 30 minutes. Excess thionyl chloride was then distilled off. The residue was briefly
20 freed from volatile compounds under an oil pump vacuum and then dissolved in 25 ml of methylene chloride, under Ar as an insert gas. The solution was slowly added dropwise to a suspension of 26 g (196 mmol) of aluminum trichloride in 60 ml of methylene chloride and the mixture was heated under reflux for a further 30 minutes. It was poured onto ice and extracted with methylene chloride. The
25 combined organic phases were dried with sodium sulfate and evaporated. The dark oily residue was chromatographed on 600 g of silica gel 60. 8.6 g (45%) of the compound 3 were able to be eluted (yellowish solid) with a mobile phase mixture of hexane/ethyl acetate (9:3).

30 Synthesis of 2-Methyl-4,5-benzoindene (4)

2.2 g (59.5 mmol) of sodium borohydride were added in portions to a solution of 7.8 g (39.7 mmol) of the indanone, compound 3 in 400 ml of a tetrahydrofuran/methanol mixture (2:1) at room temperature, and the mixture was stirred for 14 hours. The solution was poured onto HCL-acid ice and extracted
35 with ether. The combined organic phases were washed several times with water and dried with sodium sulfate. The orange-colored oil which remained after the solvent had been stripped off was dissolved in 240 ml of toluene, and the solution

was heated at 80°C with 570 mg (3.15 mmol) of p-toluene-sulfonic acid for 15 minutes. It was washed several times with water at room temperature, dried with sodium sulfate and evaporated. The residue was chromatographed on 300 g of silica gel 60. 4.7 g (65%) of the indene 4 were able to be eluted (colorless oil) with a mobile phase mixture of hexane/diisopropyl ether (20:1).
5 ¹H-NMR spectrum (360 MHz, CDCl₃): 8.02 (1,d), 7.84 (1,m), 7.59 (1,d), 7.52 (1,d), 7.38-7.48 (2,m), 7.06 (1,m), 3.42 (2,s), 2.25 (3,d).

Synthesis of Dimethylbis(2-methyl-4, 5-benzoindenyl) silane (5)
10 10.2 ml (25.5 mmol) of a 2.5 M butyllithium solution in hexane were added to a solution of 4.6 g (25.5 mmol) of the compound 4 in 50 ml of tetrahydrofuran at room temperature, and the mixture was heated under reflux for 1 hour. The red solution was then added dropwise to a solution of 1.55 g (12 mmol) of dimethyldichlorosilane in 10 ml of tetrahydrofuran at room temperature, and the
15 mixture was heated under reflux for 5 to 6 hours. The reaction solution was poured onto ice-water and extracted several times with ether. The combined organic phases were dried with sodium sulfate and evaporated, and the residue was dried under an oil pump vacuum. It was chromatographed on 300g of silica gel 60. 500 mg of unreacted starting compound 4 were initially able to be eluted with a
20 mobile phase mixture of hexane/3% ethyl acetate. The ligand system, compound 5, then followed with the same mobile phase. After the solvent had been stripped off, this ligand system was crystallized (isomers) from hexane. The yield was 1.7 g (34%, or 44% with respect to the indene, compound 4 reacted).

25 Synthesis of rac - Dimethylsilanediyibis (2-methyl-4,5-benzo-indenyl) zirconium dichloride (6)

4.0 ml (10.2 mmol) of a 2.5 M butyllithium solution in hexane were added to a solution of 1.7 g (4.1 mmol) of compound 5 in 20 ml of tetrahydrofuran at room temperature under Ar as an inert gas, and the mixture was stirred at room
30 temperature for 14 hours. The residue which remained after the solvent had been stripped off was dried using an oil pump vacuum and washed with hexane. The pale brown powder obtained was dried using an oil pump vacuum at 40 to 50°C for several hours and added to a suspension of 1.0 g (4.0 mmol) of zirconium tetrachloride in 25 ml of methylene chloride at -78°C. After the mixture had been
35 warmed to room temperature, the solvent was stripped off and the residue was extracted with 20 ml of toluene in order to remove the meso form of the metallocene, compound 6. The residue of the toluene extract was then extracted

with 40 ml of methylene chloride. The solution was concentrated to a small volume and left to crystallize at -35°C. A total of 970 mg (42%) of the ziroconcene, compound 6 were isolated in several fractions as the pure racemate.

¹H-NMR spectrum of the racemate (300 MHz, CDCl₃): 7.96 (2,m), 7.78 (2,m),
5 7.60 (2,d), 7.48-7.56 (4,m), 7.36 (2,d), 7.27 (2,s,b-Ind-H), 2.37 (6,s,Ind-CH₃),
1.36 (6,s,Si-CH₃). Mass spectrum: 574 M⁺, correct disintegration, correct isotope pattern.

The catalyst component of Example 5 was combined with methylalumoxane and supported in accordance with US 5,240,894. The activity of
10 the unsupported, methylalumoxane activated catalyst system is estimated to be 360,000 g polymer/ g metallocene/ hour. The support technique is as follows:

3000 cm³ of methylalumoxane solution (10% MAO in toluene commercially available from Witco Corporation) was added to a 37,855 cm³ (10 gallon) jacketed reactor equipped with a helical agitator. To this was added a
15 solution of 5.0 g of the dimethylsilyl(2-Me,4,5-benzoindenyl)₂ZrCl₂ metallocene in 700 cm³ of toluene. After allowing this to mix for 15 minutes, 395.9 grams of silica (Davison 948, calcined at 800 ° C for 4 hours) was added to the reactor. After mixing for 15 minutes, the toluene solvent was removed by evaporation at 65 ° C (150 °F) under vacuum. After all the solvent had evaporated, the solids
20 were held under vacuum at temperature for an additional 3 hours. The solids were slurried in isopentane, and recovered from the reactor. The solids were collected by filtration, and sparged with nitrogen to dryness. The yield of supported catalyst was 450 g.

Comparative Example 6-Prepolymerization without hydrogen of supported
25 dimethylsilyl(2-Me,4,5-benzoindenyl)₂ ZrCl₂/MAO catalyst system

The prepolymerization procedure of Example 2 was repeated using 2.5 g of the supported catalyst of Example 5. Ethylene addition was set such that the rate of prepolymerization was 0.57 g ethylene/ g catalyst solid/ hour. After 33 minutes of ethylene feed, the solids in the reactor agglomerated severely. Ethylene feed
30 was stopped after 35 minutes, and the solids were collected by suction filtration. The prepolymerized catalyst recovered contained agglomerated particles as large as 1.4 mm in diameter, and were not free-flowing. The yield of prepolymerized catalyst was 2.8 g.

Example 7-Prepolymerization with hydrogen of supported dimethylsilyl(2-
35 Me,4,5-benzoindenyl)₂ ZrCl₂/MAO catalyst system.

The prepolymerization procedure of Example 6 was repeated using 2.5 g of the supported catalyst of Example 5. The monomer feed to the reactor was a

mixture of 3.0 mol % hydrogen in ethylene. No fouling or agglomeration of the solids were observed during the 1.5 hour experiment. The prepolymerized catalyst was collected by suction filtration. The product was a granular, free-flowing solid, with no evidence of agglomerates. The yield of prepolymerized catalyst was 4.2 g.

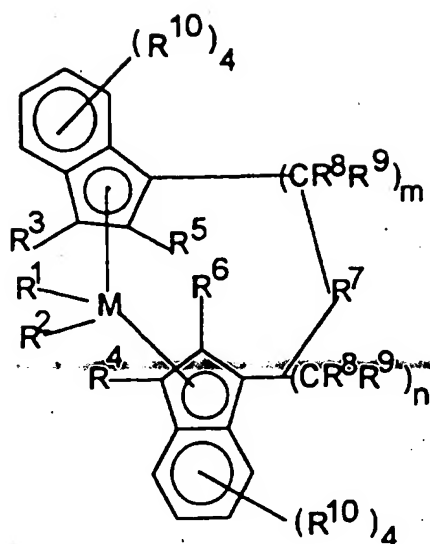
5 Example 8-Prepolymerization with hydrogen of supported dimethylsilyl(2-Me,4,5-benzoindenyl)₂ ZrCl₂/MAO catalyst system.

202.1 g of the supported catalyst made in Example 5 was slurred in 6000 cm³ in a 7,571 cm³ (2 gallon) jacketed glass reactor equipped with a helical stirrer. The reactor was chilled to a temperature of 2 ° C (36 ° F), and then the feed to the
10 reactor was initiated. For this experiment, the ethylene source was a cylinder of 1 mol% hydrogen in ethylene (commercially available and supplied by Scott Specialty Gases). The feed rate used was 1840 cm³/min. (0.065 SCFM). A total of 170,000 cm³ (6.01 SCF) were added to the reactor. During the 92 minute duration of the
15 experiment, no fouling of the reactor walls or agitator was observed. Also, there was no evidence of agglomeration of the solids in the reactor. The agitator was stopped, and the solids were allowed to settle, and the supernatant liquid was decanted. The solids were washed twice with 3800 cm³ of isopentane before collection. The solids were collected by filtration, and sparged to dryness with
20 flowing nitrogen. When dry, the prepolymerized catalyst was a granular, free-flowing solid. The yield of prepolymerized catalyst system was 350.2 g.

It should be understood that modification and variations besides those specifically disclosed and exemplified may be made without substantially departing from the scope of this invention. The form of the invention is exemplary only and not intended as a limitation of the scope thereof.

Claims:

1. A method for the prepolymerization of a supported catalyst system, said method comprising the steps of:
 - 5 (a) combining under prepolymerization reaction conditions:
 - (i) a supported metallocene catalyst system having an activity greater than 100,000 g/g/hr.; and
 - (ii) at least one alpha olefin monomer feed;
 - (b) adding hydrogen under prepolymerization reaction conditions; and
 - 10 (c) recovering a prepolymerized supported catalyst system.
2. The method of claim 1 wherein the catalyst system has an activity or greater than 150,000 g/g/hr..
- 15 3. The method of claims 1 or 2 wherein the monomer feed comprises ethylene.
4. The method of any of the preceding claims wherein the monomer feed comprises propylene.
- 20 5. The method of any of the preceding claims wherein the hydrogen is added in an amount between 0.1 to 10 mole percent relative to the monomer feed rate.
6. The method of claim 5 wherein hydrogen is added in an amount that is between 1 to 3 mole percent.
- 25 7. The method of any of the preceding claims wherein the monomer feed is added at a rate of 0.1 to 5 g olefin/g catalyst solid/hour.
8. The method of any of the preceding claims wherein the catalyst system has an activity of greater than 200,000 g/g/hr..
- 30 9. The method of any of the preceding claims wherein the catalyst system has an activity of from 150,000 g/g/hr. to 1,000,000 g/g/hr..
- 35 10. The method of any of the preceding claims wherein the supported catalyst system comprises a metallocene catalyst component represented by the formula:



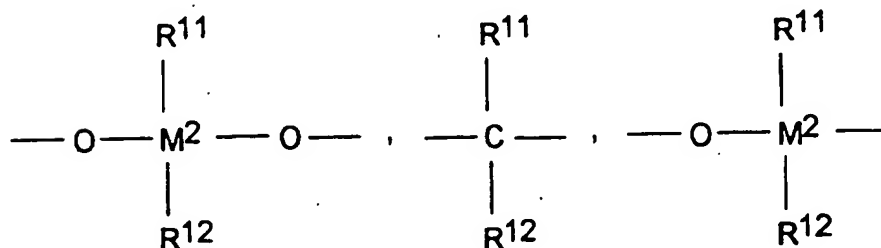
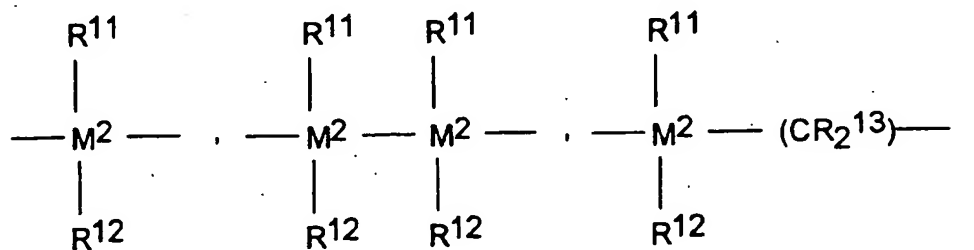
wherein M is a metal of Group 4, 5, or 6 of the Periodic Table;

R^1 and R^2 are identical or different, are one of a hydrogen atom, a C₁-C₁₀ alkyl group, a C₁-C₃ alkyl group, a C₁-C₁₀ alkoxy group, a C₆-C₁₀ aryl group, a C₆-C₁₀ aryloxy group, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, or a halogen atom;

R^3 and R^4 are hydrogen atoms;

R^5 and R^6 are identical or different, preferably identical, and are one of a halogen atom, C₁-C₁₀ alkyl group, which may be halogenated, a C₆-C₁₀ aryl group, which may be halogenated, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ -arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, a -NR₂¹⁵, -SR¹⁵, -OR¹⁵, -OSiR₃¹⁵ or -PR₂¹⁵ radical, wherein R¹⁵ is one of a halogen atom, a C₁-C₁₀ alkyl group, or a C₆-C₁₀ aryl group;

R^7 is



$=BR^{11}, =AlR^{11}, -Ge-, -Sn-, -O-, -S-, =SO, =SO_2, =NR^{11}, =CO, PR^{11},$ or
 $=P(O)R^{11},$

wherein:

- 5 R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{20} alkyl group, a C_1 - C_{20} fluoroalkyl group, a C_6 - C_{30} aryl group, a C_6 - C_{30} fluoroaryl group, a C_1 - C_{20} alkoxy group, a C_2 - C_{20} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_8 - C_{40} arylalkenyl group, a C_7 - C_{40} alkylaryl group, or R^{11} and R^{12} , or R^{11} and R^{13} , together with the atoms binding them, can form
 10 ring systems;

M^2 is silicon, germanium or tin;

R^8 and R^9 are identical or different and have the meanings stated for R^{11} ;

m and n are identical or different and are zero, 1 or 2, preferably zero or 1,

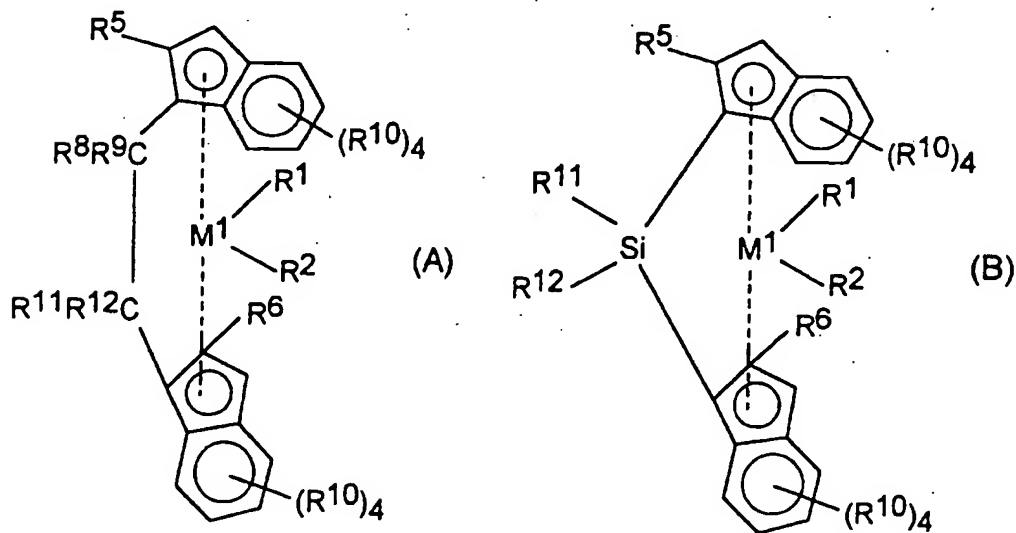
m plus n being zero, 1 or 2, preferably zero or 1; and

- 15 the radicals R^{10} are identical or different and have the meanings stated for R^{11}, R^{12} and R^{13} ; two adjacent R^{10} radicals can be joined together to form a ring system.

11. The method of claim 10 wherein M^2 is silicon.

20

12. The method of any of the preceding claims wherein the metallocene catalyst system comprises a metallocene component represented by the formula:



25

wherein:

M^1 is Zr or Hf, R^1 and R^2 are methyl or chlorine, and $R^5, R^6, R^8, R^9, R^{10}, R^{11}$ and R^{12} have the meanings as defined in claim 10.

INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/US 96/02300

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/609

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 598 543 (MITSUBISHI PETROCHEMICAL CO) 25 May 1994 see claims; see page 10, lines 20-22; page 8, line 22 to page 9, line 4 ---	1-4
A	EP,A,0 279 586 (MITSUI PETROCHEMICAL IND) 24 August 1988 see claims; see page 12, lines 35-37 ---	1-12
A	EP,A,0 442 725 (MITSUI PETROCHEMICAL IND) 21 August 1991 see claims; see page 7, lines 4-10 ---	1-12
A	EP,A,0 354 893 (FINA TECHNOLOGY) 14 February 1990 see claims; see page 4, lines 11-34 --- -/--	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

30 May 1996

Date of mailing of the international search report

24.06.96

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INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 96/02300

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 012, no. 482 (C-553), 15 December 1988 & JP,A,63 199206 (MITSUI PETROCHEM IND LTD), 17 August 1988, see abstract</p> <p>-----</p>	1-12

INTERNATIONAL SEARCH REPORT

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